PB-216 362

TASTE AND ODOR PRODUCING COMPONENTS IN PETROLEUM REFINERY GRAVITY OIL SEPARATOR EFFLUENTS

C. C. Ruchhoft, et al

Environmental Health Center
Cincinnati, Ohio

March 1953

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 216 362

LIBRARY
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

Department of
Health, Education, and Welfare
Public Health Service
Environmental Health Center
Cincinnati, Ohio
March 1953

TASTE AND ODOR PRODUCING COMPONENTS IN PETROLEUM REFINERY GRAVITY OIL SEPARATOR EFFLUENTS

Details of illustrations in this document may be better studied on microfiche.

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

by

C. C. Ruchhoft, Sanitary Engineer Director
F. M. Middleton, Chemist
Harry Braus, Chemist
Aaron A. Rosen, Chemist

TASTE AND ODOR PRODUCING COMPONENTS IN PETROLEUM REFINERY GRAVITY OIL SEPARATOR EFFLUENTS*

The control of tastes and odors in drinking waters obtained from surface water sources is a major problem in water purification. Tastes and odors in surface waters may come from aquatic plants such as algae natural land drainage, and the discharge of domestic sewage and industrial wastes. The odor bearing materials, largely organic, may undergo physical and chemical changes as a result of sedimentation, vaporization, oxidation, temperature and light effects, and biochemical action.

This study was undertaken to determine the types and quantities of materials present in petroleum refinery gravity oil separator effluents that contribute to taste and odor when discharged into surface waters used as drinking water sources.

Petroleum refineries universally separate slop oils from waste waters by gravity differential-type separators. Such waste oils originate from processing operations, spills, leaks, tank draw-offs, and maintenance and repair activities. Operating experiences with gravity oil separators have been adequately described in the literature[10,6]. Although the purpose of the separators is to break emulsions and separate the oil, this separation is not complete and oil separator effluents contain materials in solution, emulsion, and suspension. The effluent is usually discharged without additional treatment.

(*) Presented before the 123rd National Meeting of the American Chemical Society, Los Angeles, California, March 15-19, 1953

SAMPLES

SOURCES

Samples were collected from five petroleum refineries, all operated by different companies, selected to represent a reliable cross-section of the refining industry. No attempt was made to correlate the types of crude oil processed or the products manufactured with the waste materials in the oil separator effluents. Refinery A is a very large, complete refinery. Refinery E is the smallest of the five and performs only thermal cracking. In addition, certain of the stronger wastes at Refinery E are not disposed of through the oil separator. Refineries B, C and D are intermediate in size.

APPARATUS AND PROCEDURES

Carbon Filter Method — Most of the samples were collected by passing 100 or more gallons of oil separator effluent through a small active carbon filter[2,1] at a rate of 2 to 6 gallons per square foot per minute. The materials adsorbed on the carbon were eluted by means of chloroform in a Soxhlet type extractor and recovered by distillation of the solvent.

One filter system consisted of 4-inch iron pipes, 3 feet in length, filled with granular active carbon (Cliffchar 4-10 mesh, Cliffs Dow Chemical Company). The carbon filter was preceded by a sand filter which was backwashed at intervals to prevent clogging of the carbon. Losses on backwashing and mechanical entrainment of oily materials in the sand filter resulted in low recoveries by this method.

An improved system of filters, consisting, of pyrex glass cylinders 3 inches in diameter and 18 or 36 inches in length, was adopted for later studies. The prefilter contained granular carbon and the second filter contained Nuchar C-190* unground active carbon. The C-190 carbon was found to be more active than the granular carbon but clogged easily if suspended material was present in the sample. This filter system was used successfully without back-washing when 500 gallons or less of oil separator effluent was filtered. The assembled pyrex filter and the details are shown in Figures 1 and 2.

The results of comparative studies made on refinery B effluent with sand and carbon prefilters and C-190 carbon filters in series are shown in Table 1. The effluent was filtered under a pressure of 40 to 50 psi during this test. Figure 3 shows diagrammatically the filter systems used in the study.

The data in Table 1 indicate that the prefilter removes approximately one-half of the total quantity of organic materials recovered from both filters. Sand appeared to be as effective as granular carbon in these tests suggesting that the removal of these substances by the prefilter is largely mechanical. Filters operated in parallel yielded equivalent quantities of material. Table 2 shows the yields obtained from the various refinery effluents.

(*) Product of Industrial Chemical Sales Division, West Virginia Pulp and Paper Company, New York, New York

The carbon filter technique does not give quantitative recovery of organic material in oil separator effluents. The filter may lose adsorption capacity by becoming coated with silt, iron rust, or other suspended matter. Under the operating conditions described, two carbon filters in series adsorbed approximately 90 per cent of the organic material in the influent sample. Chloroform extraction does not recover all of the adsorbed materials. Evidence from present studies indicates that materials recovered from the carbon filter are representative of the organic components of the waste effluent if the filter is operated to avoid saturation of the carbon. Any low-boiling odorous materials adsorbed by the carbon are lost through distillation with the chloroform. For example, volatile mercaptans were shown to be present in the distillate. Mercuric chloride complexes were obtained by extraction of the chloroform distillate, diluted with hexane. The present study has been limited to those substances that are not distilled with the chloroform.

Liquid-Liquid Extraction — During the course of the investigation liquid-liquid extraction methods utilizing countercurrent flow[7] were applied to oil separator effluent samples from refinery B. Composite samples of the aqueous effluent were extracted at a pH of 3.0 ± 0.5 with diethyl ether as the continuous phase. A diagrammatic sketch of the type of extractor used is shown in Figure 4. The organic residue is recovered by distillation of the ether. Liquid extraction methods are more quantitative and simpler to use than the carbon filter. Basic materials are recovered by an additional extraction at high pH. The present method is not suitable for extraction of large volumes of extremely dilute waste effluents.

Oil separator effluents vary widely in organic content from day to day. Recoveries from refinery E by liquid extraction methods on samples collected on different days were 81 p.p.m., 481 p.p.m., 68 p.p.m., and 155 p.p.m. Liquid extraction of the acidified waste recovers the organic materials almost quantitatively. The organic acids which exist as salts in alkaline or neutral solutions are extracted by this method. Hence the total recovery from acidified solutions is greater than from alkaline or neutral samples. In general, saturation of the aqueous phase with sodium chloride increases the extraction efficiency. The salt also appears to prevent troublesome emulsions from forming.

EXAMINATION OF EXTRACTS

SEPARATION OF GROUPS AND FRACTIONAL DISTILLATION

The recovered extract was a complex liquid with a refinery-like odor. Although it is not feasible to separate such a mixture into all of its components, separations by groups can be accomplished and certain individual constituents may be identified. Neutral, phenolic, acidic and basic groups were separated from the mixture by use of differential solubility methods[2,1]. Table 3 shows the quantities of the various groups recovered from the oil separator effluent extracts. Losses of 7 to 15 percent of the material taken for separation represent unrecovered groups, ether insoluble materials and manipulatory losses.

Various quantities of elemental sulfur, ranging from 0.0 to 27.6 percent, separated from the organic extracts upon removal of the chloroform, as shown in Table 2. Laboratory tests showed that sodium

sulfide solutions yield free sulfur when subjected to the carbon filter technique, thus offering an acceptable explanation for the occurrence of elemental sulfur in refinery effluent extracts. Because of the high proportion of free sulfur in Refinery D waste extract and the relatively small amount of extract obtained, group separation of this sample was not performed.

The neutral group of compounds constituted the major portion (58 to 85 percent) of the extract and possessed an odor typical of the entire extract. The material was separted into five fractions by vacuum distillation to permit more detailed study of the composition and odor characteristics of the neutral compounds. The percentage of material separated in each fraction and the boiling point range of the fractions are shown in Table 4. Exact fractionation was not attempted. Arbitrary boiling point ranges were used in all distilla tions for purposes of comparison of the various extracts.

Phenolic compounds were present in the extracts in quantities ranging from 0.6 to 24.7 percent. Sample B-1, Table 3, showed an unusually large amount of phenol compared to other samples at the same refinery and other refineries. This may have been caused by an unusual discharge of phenol by the plant during the filter operation. Sample B-2, collected at the same refinery a few days later, contained only 1.3 percent of phenol.

Organic acids were recovered from the extracts in quantities of 2 percent or less in samples collected by the carbon filter. However, sample E-2, which was recovered by liquid extraction of the acidified waste, yielded 11 percent of acids. Organic basic materials were present in quantities ranging from 0.3 to 4.5 percent.

Table 4 shows the density, refractive index, and the percentage yield of material separated in each distillate fraction of the neutral groups. These values reveal differences between the various refinery waste effluents.

The yields, refractive indices and densities of the distillate fractions of samples E-1 and E-2 are very similar. Sample E-1 was obtained by the carbon filter method. Sample E-2 was obtained by liquid extraction from the same refinery effluent although the times of collection did not coincide. This evidence and the information obtained from infrared spectra, indicate that neutral materials recovered from the oil separator effluent by the carbon filter and by liquid extraction methods are similar

INFRARED SPECTRA

The infrared spectra of all the recovered neutral groups were recorded. Similarly, the spectrum of each neutral fractional distillate was obtained. The instrument used was a Baird double beam recording spectrophotometer, the cell path length in each case being 0.05 mm. Figure 5 is the infrared spectrum of the neutral fraction of the carbon filter extract from refinery E, the smallest of the refineries included in this study. Figure 6 is the spectrum of the corresponding group from refinery A, the most diversified of the five investigated.

Both curves reveal predominantly the characteristics of hydrocarbons, with the strongest bands at 3.4, 6.8, and 7.3 μ, which are due to C-H groups. The OH absorption at 3.0 μ is negligible. Weak carbonyl absorption at 5.9 μ is evident, being significantly stronger in Figure 5.

A band at 6.2 μ, attributed to phenyl groups, is stronger in Figure 6. The more aromatic character of refinery A material is further demonstrated by the stronger bands in the 12.0-14.5 μ region. Conversely, in Figure 5, the band at 13.8 μ, due to long chain aliphatics, is stronger than in Figure 6.

The spectra of the neutral groups recovered from the other refineries were similar to the two illustrated. They resembled Figure 6 more closely than Figure 5, showing both less oxygen content and greater aromatic character than the refinery E material. The discussion of the spectra of the distilled fractions of the neutral groups is similarly limited to refineries A and E. These spectra showed only the bands present in the original neutral group, thus indicating the absence of chemical change during the distillation. The characteristic differences described for the spectra of the whole neutral group were also evident in the spectra of the individual distilled fractions.

Figure 7 is the infrared spectrum of distilled fraction 1 of the neutral group fo refinery A. This fraction is of interest because of its representative low threshold odor concentration, as shown in Table 5. Strong evidence for the identities of some of the components of this fraction is provided by the infrared spectrum. The compounds and identifying bands are:

Toluene, 13.7, 14.4 μ

o-Xylene, 8.9, 9.5, 9.8, 13.5 μ

m-Xylene, 8.55, 9.1, 9.6, 11.05, 11.4, 13.0, 14.5 μ

p-Xylene 5.3, 12.6 μ

A band at 12.8 μ suggests naphthalene or substituted naphthalenes. The same band is predominant in the same region of the spectrum of distilled fraction 2. However, the ultraviolet spectrum of this fraction showed that naphthalene is only a minor component of fraction 2, therefore the band at 12.8 μ cannot be attributed to naphthalene. The ultraviolet spectrum resembled, instead, 2,7-dimethylnaphthalene. Fraction 1 was the only one which failed to yield a urea adduct (11), thus supplying additional evidence of its aromatic nature.

The spectra of the higher-boiling refinery A fractions showed progressively less marked aromatic bands and did not permit identification of individual components. The spectra of the refinery B distilled fractions indicated these materials to be less aromatic in character than the fractions of refinery A. Identification of individual components was not accomplished.

ODOR STUDIES

METHODS

The standard procedure(9) was modified to determine the threshold odor concentrations (T.O.) of the raw extracts, the various groups, and the fractional distillates of the neutral groups. Stock solutions of 5 to 10 p.p.m. concentration were prepared by dispersing each sample in odor-free water, using a mechanical shaker. Suitable dilutions of each stock solution were prepared in concentrations encompassing the T.O. In this range, each successive concentration was reduced by a factor of 0.5. These series, together with randomly-spaced blanks, were judged by a panel of observers. The minimum concentration

in the series where each observer's responses became consistently correct was taken as his threshold. The geometric mean of all observers' threshold values was recorded as the T.O. of the sample.

"Taste" properties of virtually all organic substances in water are actually odor properties, although the levels of threshold perception may differ. Taste tests were not performed, since for our purposes, it was considered that the odor tests constituted a satisfactory index of problems that may arise from discharge of these wastes into drinking water sources.

RESULTS

Table 5 gives the maximum, minimum and geometric averages of the threshold odor determinations. The average* T.O. of the total extracts varied from 25 to 52 p.p.b. The average T.O. on the acidic groups ranged from 0.014 to 24 p.p.b. The average T.O. of the phenolic groups varied from 28 to 225 p.p.b. The average T.O. of the neutral groups ranged from 19 to 64 p.p.b. and the average T.O. of the five distillation fractions of the neutral groups were respectively 9-16 p.p.b., 10-37 p.p.b., 15-29 p.p.b., 9-91 p.p.b. and 220-8000 p.p.b.

PROPERTIES OF ODOROUS COMPONENTS

Identification of the specific components causing odor in water containing refinery wastes would substantially assist those concerned with waste disposal and water purification. Because of relative abundance,

---

(*) Geometric average is meant wherever average is referred to in connection with odor thresholds.

odor intensity and odor characteristics, it is evident that the neutral group is generally the most significant source of odor problems among refinery waste components. Since it has been shown that this group consists primarily of hydrocarbons, it is noteworthy that such compounds are among the most persistent in relation to natural stream and waterworks purification processes.

The data presented to this point do not rule out the possibility that a relatively small proportion of very odorous components, accompanying the hydrocarbons, may be the actual source of odor in the neutral groups. Indeed, the general occurrence and pronounced odor of sulfur compounds, especially mercaptans, in petroleum, suggest that this class of compounds may be the true odor-bearers. It should be noted from Table 5, however, that the odor is distributed fairly uniformly in the distillable portions of the neutral groups. The fact that the odor is not concentrated in a single boiling range indicates that the odorous components, if not hydrocarbons, have boiling ranges very comparable to the distillable hydrocarbons.

Further attempts were made to remove the postulated odorous components from the hydrocarbon bulk of the neutral groups. For this purpose, a portion of the neutral group separated from refinery B effluent was extracted with mercuric chloride solution[8], to remove mercaptans and certain other sulfur compounds. By this method, the sulfur content was reduced from 3 to 2.5 percent, and a mercaptan-like component of the odor also disappeared. Nevertheless, no significant change in T.O. was accomplished by this step.

In another approach, a portion of the mercuric chloride-treated neutral group was chromatographed on activated alumina. Iso-octane eluted 76 percent of the sample as a colorless oil, shown by the infrared spectrum to consist almost entirely of aliphatic hydrocarbons. Benzene eluted 19 percent of the sample, which was aromatic. The T.O. and sulfur contents of these fractions, the original neutral group, and the neutral group after treatment with mercuric chloride, were:

	S, percent	Av. T.O. conc., D.B.b
Neutral group	3.0	19
Neutral group, $HgCl_2$-treated	2.5	12
Aliphatic fraction	0.42	21
Aromatic fraction	5.4	9

The chromatographic procedure generally removes the more polar sulfur, nitrogen, and oxygen compounds. The increased sulfur content of the aromatic fraction is probably due to substituted benzothiophenes[8] which are not retained by alumina. Qualitative and quantitative odor characteristics of the aromatic fraction suggest cyclic sulfur compounds to be important contributors of odor to refinery wastes. Relative abundance and high odor intensity establish the aliphatic fraction as the major source of odor in the neutral group. These results, however, do not reveal the extent of odor contribution by the hydrocarbon components of this fraction.

ODORS OF PHENOLIC, BASIC AND ACIDIC GROUPS

Phenols occur in refinery wastes in significant quantities as shown in Table 3. Their effects on taste and odor in drinking water sources have been extensively investigated. Problems due to the discharge of phenols, in contrast to neutral compounds, are diminished because the materials are amenable to treatment within the plant, are subject to chemical and biological oxidation,[4,3] and effective water treatment methods for them exist.

Organic acidic materials were usually recovered in quantities of 2 percent or less by the carbon filter. The liquid extraction technique under acid conditions recovered 11 percent of acidic materials (Sample R-2, Table 3). The odor intensity of these materials was high and in concentrated form resembled the odor of black walnuts. One exceptional sample showed a T.O. of 14 parts per trillion. The role of acidic refinery compounds in causing taste and odor in drinking water has not yet been determined.

Organic bases were not recovered in large quantities by the methods used in this study. Preliminary studies of the amines recovered indicated they are largely of the pyridine type. Additional research is being conducted to further clarify the role of these materials in taste and odor problems.

EFFECT OF ODOR PROPERTIES ON DISPOSAL PROBLEMS

Objectionable odors do not necessarily have the lowest threshold odor concentrations. Qualitative characteristics as well as the dilution required must be considered in the total taste and odor problem.

However, drinking water should be free of any odor and the threshold is the usual criterion of acceptability. Water consumers may tolerate water somewhat above threshold taste and odor levels by repeated subjection to it.

Calculations using values from the results of this study indicate the extent of possible taste and odor contributed by refinery wastes. It has been shown that 50 p.p.m. is an average value of the concentration of organic materials in oil separator effluents. A reasonable average T.O. of the total extract is considered to be 50 p.p.b. On this basis, 0.417 pounds of the chemicals would produce odor in one million gallons of water and one billion gallons of water would be required to dilute each million gallons of waste to the threshold odor level. This indicates that a factor of 1000 is required for dilution. This figure appears conservative. According to Giles(5) the average threshold odor number of oil separator wastes is 16,000, meaning 16 billion gallons of dilution for each one million gallons of waste. Considering that small refineries may discharge waste in amounts of 5 to 10 mgd, the magnitude of the potential taste and odor contributions of these wastes is obvious.

Physical, chemical and biological action in the receiving waters generally tend to reduce or alter the odorous properties of these materials. However, these natural forces are often unable to cope with the various conditions imposed on them and serious problems result. Satisfactory procedures for elimination or removal of these constituents to acceptable levels in surface drinking water sources remain to be developed. Consequently, those concerned with water purification must understand the problems involved and should undertake and support research on the solution of these problems.

SUMMARY

1. Organic materials were concentrated from the gravity oil separator effluents of five petroleum refineries, using carbon filters and countercurrent liquid-liquid extraction.

2. The recovered extracts were examined by means of group separations, fractional distillation, infrared absorption spectrophotometry, chromatography, and organoleptic procedures to determine the kinds and quantities of organic materials in petroleum refinery wastes that may give rise to taste and odor in receiving waters used for drinking water sources.

3. The neutral group, consisting mainly of aliphatic and aromatic hydrocarbons, was found to be the principal source of odorous materials in these wastes. Neutral sulfur compounds, associated largely with the aromatic materials, add substantially to the odor characteristics. Phenolic compounds, the second most abundant group in these wastes, are significant in problems of taste and odor. The role of acidic and basic materials as contributors to taste and odor in finished water is believed to be less important.

ACKNOWLEDGMENT

Thanks are due Robert C. Kroner and John M. Inskeep for assistance with the analytical tests; also it is wished to acknowledge the assistance given by R.R. Hopkins, P.J. Launer, and R.J. Austin in the interpretation of infrared spectra.

Literature Cited

(1) Braus, Harry, Middleton, F.M., and Ruchhoft, C.C.
Anal. Chem. 24, 1872 (1952).

(2) Braus, Harry, Middleton, F.M., and Walton, Graham
Anal. Chem. 23, 1160 (1951).

(3) Ettinger, M.B., Moore, W. Allan, and Lishka, R.J.
Indust. and Eng. Chem. 43, 1132 (1951).

(4) Ettinger, M.B., and Ruchhoft, C.C.
Indust. and Eng. Chem. 41, 1422 (1949).

(5) Giles, R.N.
Sew. and Indust. Wastes 24, 1495 (1952).

(6) Giles, R.N., Scheineman, F.W., Nicholson, C.T., and Austin, R.J.
Sew. and Indust. Wastes 23, 281 (1951).

(7) Middleton, F.M., Braus, Harry, and Ruchhoft, C.C.
Proc. Seventh Industrial Waste Conf., Purdue Univ., Lafayette, Ind. May 7 - 9, 439 (1952).

(8) O'Donnell, C.
Anal. Chem. 23, 894 (1951).

(9) Standard Methods for the Examination of Water and Sewage, Ninth Ed., Amer. Public Health Assn., p. 16, New York, New York, (1946).

(10) Weston, Roy F.
Indust. and Eng. Chem. 42, 607 (1950).

(11) Zimmerscheid, W.J., Dinerstein, R.A., Weitkamp, A.W., and Marschner, R.J.
Indust. and Eng. Chem. 42, 1300 (1950).

Table No.1

Filter Operation Data and Recovery of Organic Chemicals from Oil Separator Effluent of Refinery B

Sample No.	Prefilter					Final Filter[a]			Organic Extracts Recovered				
									Prefilter		Final Filter		Total
	Type of Filter	Rate of Flow gal/ sq. ft./ min.	Depth of Filter	Total Flow	Back-washed	Rate of Flow gal/ sq.ft./ min.	Depth of Filter	Total Flow					
			Inches	Gallons			Inches	Gallons	grams	p.p.m.	grams	p.p.m.	p.p.m.
B-1	Sand	6	24	318	No	5.0	18	154	53.5	44	24.9	43	87
		-	-	-	-	5.0	18	164			27.2	44	88
B-2	Granular Carbon	4	24	1530	Yes	2.5	18	790	88.0	15.2	48.4	16.2	31.4
		-	-	-	-	2.5	18	740			51.1	18.2	33.4
B-3	Granular Carbon	5	18	84	No	5.0	18	84	4.3	13.5	2.5	7.8	21.3
B-3a	Sand	5	18	81	No	5.0	18	81	4.8	15.7	1.8	5.9	21.6
B-4	Granular Carbon	5	18	85	No	5.0	18	85	8.6	26.7	12.5	38.5	65.2

(a) Final filters contained Nuchar C-190 unground carbon

Table No. 2

Recovery of Chloroform Extractable Materials from Oil Separator Effluents by Carbon Filter Technique

Refinery	Sample No.	Type of[a] Prefilter	Rate of Flow gal/sq.ft./min.	Depth of Carbon	Quantity of Effluent Filtered	Recovery of Chloroform-Extractable Materials		
								Free Sulfur
				Inches	Gallons	Grams	p.p.m.	percent of extract
A	A-1	Sand	3.0	24	7,500	369	13.0	0.00
	A-2	Granular Carbon	2.3	42	309	39.3	33.5	1.4
B	B-1	Sand	5	30	500	35.0	18.5	13.4
	B-2	Sand	5	30	2,000	112	14.8	5.4
	B-3	Granular Carbon	2.5	48	500	137	72.0	1.4
C	C-1	Sand	4.2	18	2,080	59	7.5	0.0
D	D-1	Granular Carbon	2.5	48	320	17.4	14.4	27.6
E	E-1	Sand	5.0	18	154	78.4	87.0	0.00

(a) Sand prefilters were not extracted. Granular carbon prefilters were extracted.

Table No. 1

Percentage Recovery of Neutral, Phenolic, Acidic and Basic Groups from Oil Separator Effluents[a]

Refinery	Sample No.	Neutral Group Percent	Phenolic Group Percent	Acidic Group Percent	Basic Group Percent	Loss Percent
A	A-1	84.5	3.7	0.15	0.44	11.2
	A-2	78.5	4.5	1.0	1.0	15.0
B	B-1	57.5	24.7	1.9	1.4	10.9
	B-2	85.0	1.3	0.5	4.4	9.1
	B-3	85.0	4.2	0.3	0.4	9.3
C	C-1	87.5	0.6	0.2	4.5	7.2
E	E-1	64.0	1.1	0.9	0.33	33.6[b]
	E-2	87.4	0.7	11.1	—	0.8

(a) Sample E-2 was obtained by liquid extraction.
All others were obtained by carbon filter technique.

(b) Excessive loss unaccounted for.

Table No. 4

Fractional Distillation of Neutral Fractions of Petroleum Wastes

Sample	A-2			B-3			C-1			E-1			E-2		
	Per-Cent	D_4^{20}	N_D^{20}	Per-Cent	D_4^{20}	N_D^{20}	Per-Cent	D_4^{20}	N_D^{20}	Per-Cent	D_4^{20}	N_D^{20}	Per-Cent	D_4^{20}	N_D^{20}
Whole Neutral	—	0.890	1.496	—	0.877	1.488	—	0.925	1.524	—	0.895	1.491	—	0.903	1.504
Fract. I[(a)]	15.6	0.848	1.4768	4.5	0.834	1.4665	41.5	0.889	1.5099	1.8	0.845	1.4636	0	—	—
" II	23.5	0.874	1.4905	21.1	0.842	1.4715	21.3	0.926	1.5330	13.4	0.840	1.4763	13.6	0.846	1.4742
" III	9.2	0.891	1.4988	25.0	0.850	1.4761	6.9	0.917	1.5174	15.8	0.863	1.4795	15.5	0.859	1.4796
" IV	10.3	0.899	1.5001	12.5	0.866	1.4841	3.5	0.918	1.5110	6.4	0.860	1.4795	5.6	0.870	1.4861
" V	38.4	—	1.509	33.0	—	1.515	16.0	—	—	58.4	—	1.502	57.1	—	1.525

21

(a) Boiling ranges:

I: <110°C. @ 10 mm. Hg
II: 110-145°C. @ 10 mm. Hg
III: 145-160°C. @ 10 mm. Hg
IV: 160-170°C. @ 10 mm. Hg
V: Residue

Table No. 5

Threshold Odor Concentrations of Oil Separator Effluent Extracts

Threshold Odor Concentration[a] - Parts per Billion

Refinery	A			B			C			D					
Sample No.	A-2			B-3			C-1			D-1			D-2		
Sample Source	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
Total Extract	64	16	25	128	16	37	64	16	32	64	16	28	256	16	52
GROUPS															
Acidic	0.016	0.008	0.014	8	8	8	32	16	24	8	2	4	32	8	15
Basic	16	8	14	256	32	86	32	8	18	512	64	212	-	-	-
Phenolic	32	16	28	256	64	90	256	64	98	128	32	54	320	160	225
Neutral Fractions	32	16	25	64	16	32	128	4	19	64	8	26	128	32	64
1	16	8	11	-[b]	-	-	32	4	16	16	4	9	-	-	-
2	64	2	17	-	-	-	32	8	23	16	8	10	128	16	37
3	32	2	16	-	-	-	32	8	15	64	8	29	128	8	27
4	16	4	9	-	-	-	32	8	20	128	2	26	128	64	91
5	512	64	220	-	-	-	-	-	-	2560	160	840	10,000	5120	8000

a - Threshold tests were run by a panel of 4 to 7 observers and the geometric mean computed.

b - No odors on fractions because of partial decomposition during distillation.

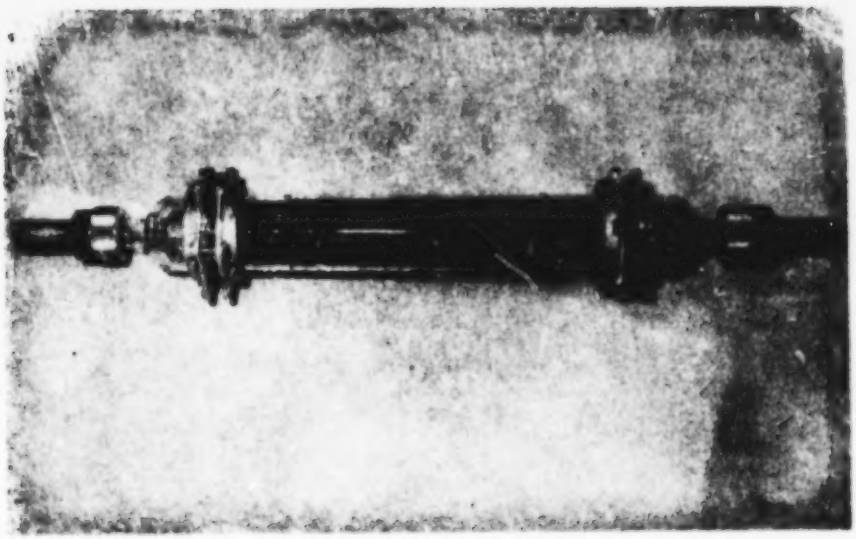


FIG. 1. CARBON FILTER CONSTRUCTED OF PYREX GLASS

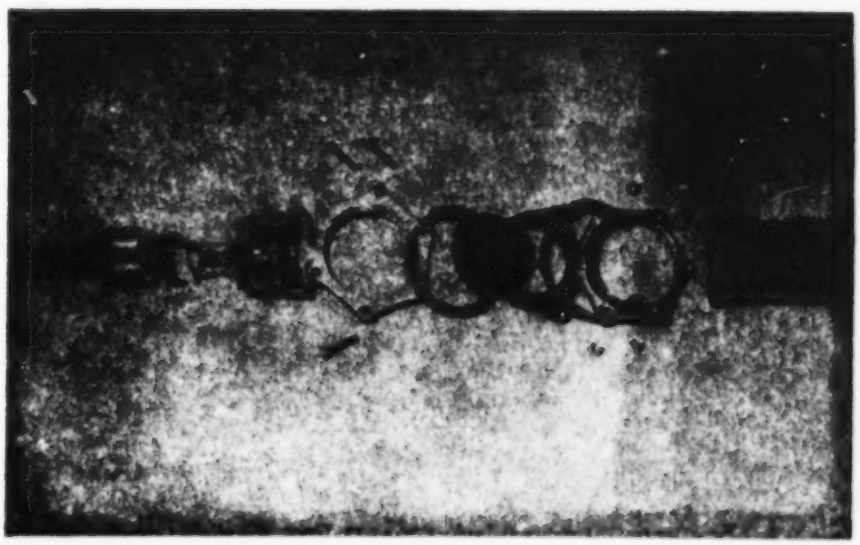
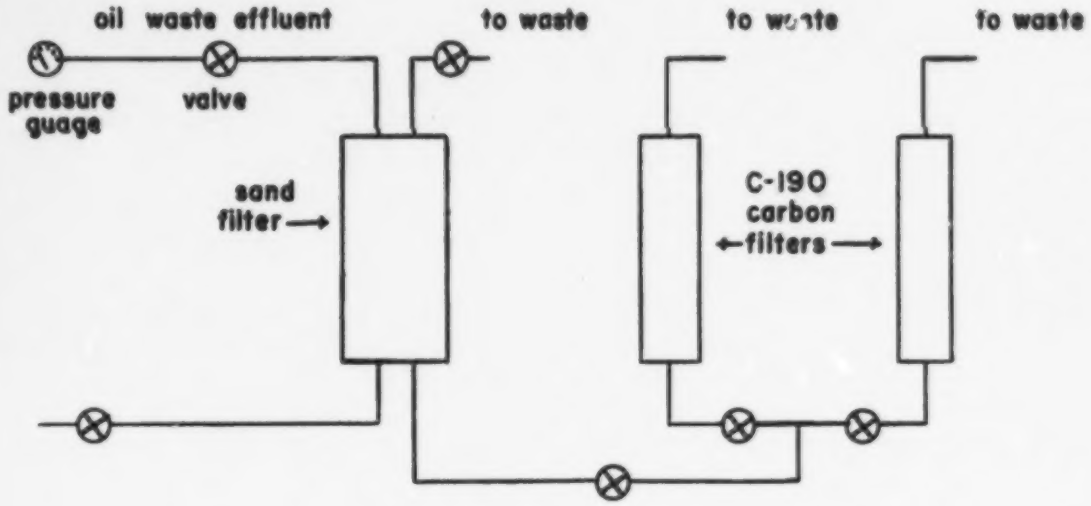
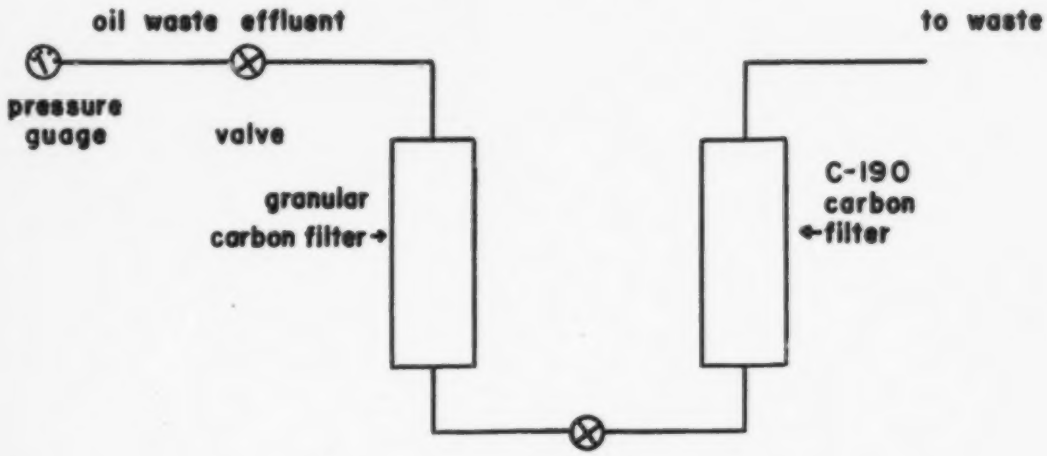


FIG. 2. DISASSEMBLED VIEW OF PYREX CARBON FILTER



FILTER SYSTEM A[a]

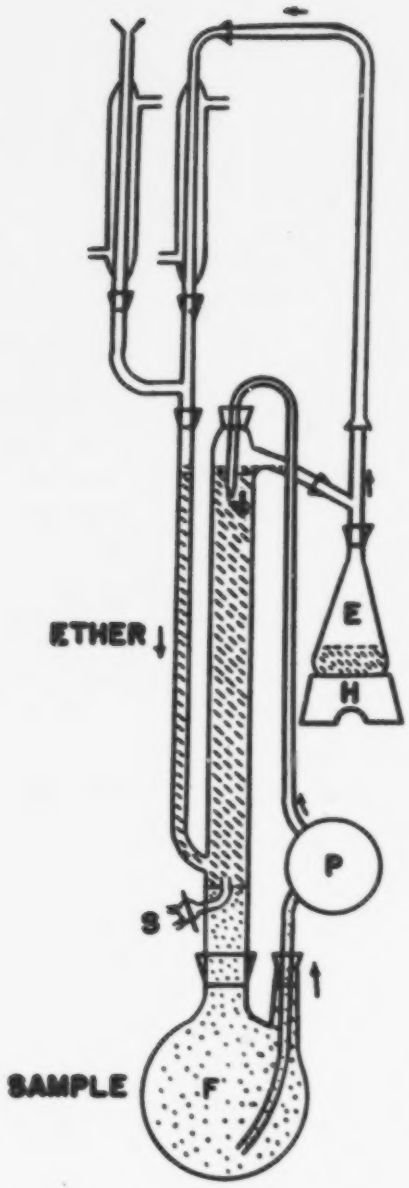


FILTER SYSTEM B[b]

a. Used in experiment NO. 1
Experiment NO. 2 - Granular carbon filter replaced sand filter

b. Used in experiments 3 and 4
Experiment 3a - Prefilter contained sand instead of granular carbon

FIGURE 3-Schematic Diagram of Carbon Filter Systems



E- ETHER FLASK
F- SAMPLE FLASK
H- HEATER
J- JET TIP
S- 3-WAY STOP COCK
P- CIRCULATING PUMP

CONTINUOUS COUNTERCURRENT EXTRACTOR

FIGURE 4

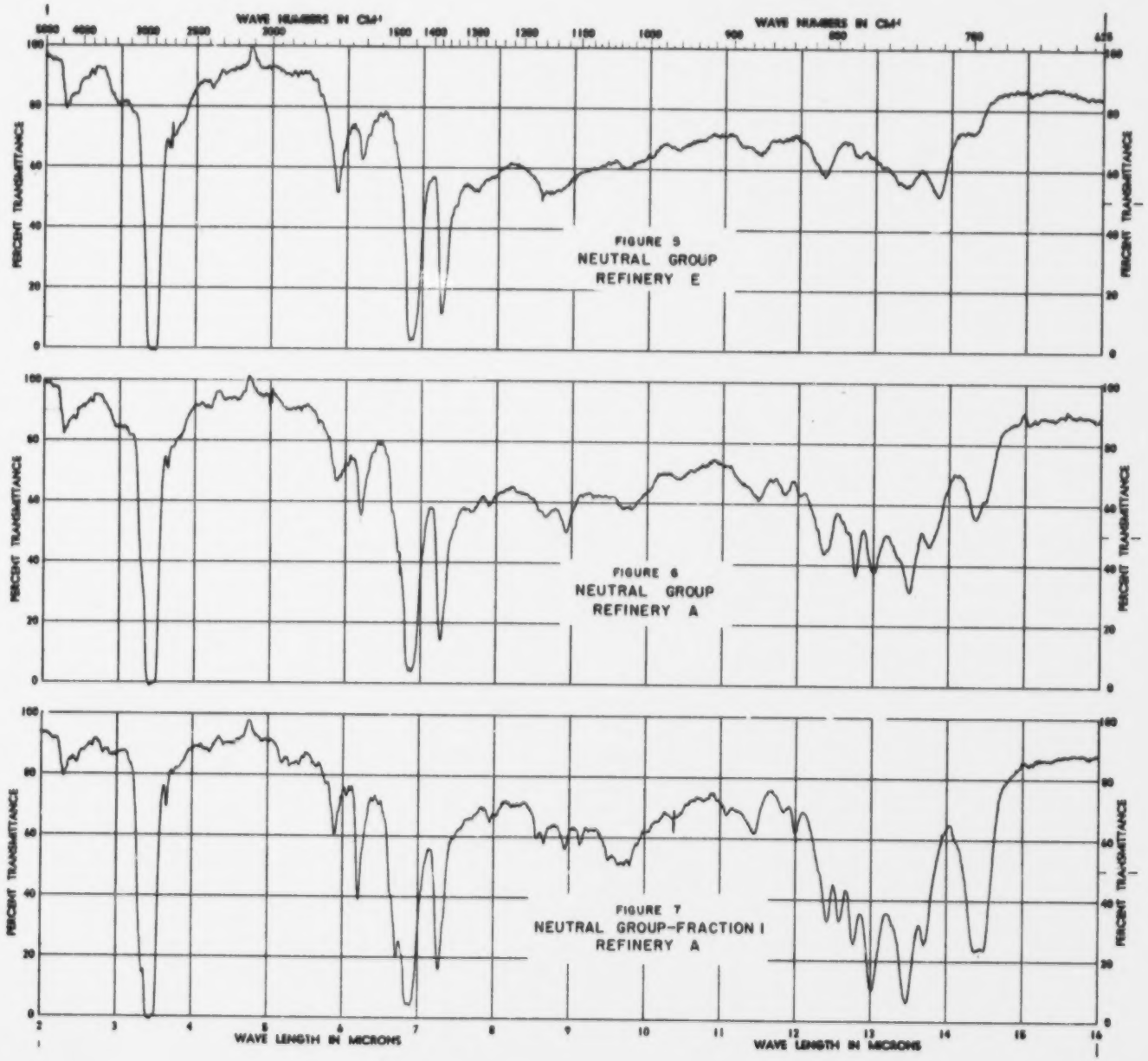


FIGURE 9
NEUTRAL GROUP
REFINERY E

FIGURE 6
NEUTRAL GROUP
REFINERY A

FIGURE 7
NEUTRAL GROUP–FRACTION I
REFINERY A